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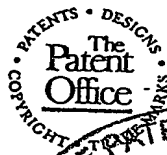
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9647

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BP EXPLORATION OPERATING COMPANY LIMITED
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Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

6225916002

4. Title of the invention

PROCESS

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PROCESS

This present invention relates to scale inhibitors and their use. Scale inhibitors are used in production wells to stop scaling in the formation and/or in the production lines down hole and at the surface.

Scale is a slightly soluble inorganic salt, such as barium or strontium sulphate, calcium carbonate, calcium sulphate or calcium fluoride. In the production of hydrocarbons from these subterranean formations the deposition of scale on surfaces and production equipment is a major production problem. Scale build-up decreases permeability of the formation, reduces well productivity and shortens the lifetime of production equipment. In order to clean scaled-up wells and equipment it is necessary to stop the production i.e. by killing the well which is time-consuming and costly.

Scale formation can be reduced by the introduction of inhibitors into the formation. US 5,089,150 relates to a method of extending the life of a scale inhibitor by cross-linking an inhibitor with a polyalcohol. The scale inhibitor includes carboxylated polymers, phosphorus-containing materials such as organophosphates, organophosphonates and polyphosphonates. Said carboxylated polymer contains either wholly or partially, an alpha, beta olefinically unsaturated carboxylic acid with a molecular weight of 200 to 20,000. The organophosphorus-containing inhibitors include alkyl ethoxylated phosphates; ethylenediaminetetramethylene phosphonic acid; aminotrimethylene phosphonic acid; hexamethylenediaminetetramethylene phosphonic acid; diethylenetriaminepentamethylene phosphonic acid; hydroxyethylidene diphosphonic acid and polyvinyl phosphonic acids. Polyacrylic acid and phosphino polyacrylic acid having a molecular weight of about 1,000 to about 5,000 are preferred

scale inhibitors. Polyalcohols which can be utilized are those having two or more hydroxyl functions. Exemplary polyalcohols include ethylene glycol, glycerol, and polyvinyl alcohols. Cross-linking occurs by esterification of the carboxylic acid in the inhibitor with the hydroxyl groups in the polyalcohol which results in a large molecular weight increase. In the case of an organophosphorus-containing inhibitor, cross-linking occurs by esterification of the phosphoric or phosphonic acid in the inhibitor with the hydroxyl group in the polyalcohol. The increased molecular weight of the cross-linked inhibitor enhances its retention in subterranean formations. When the desired molecular weight or viscosity has been obtained, the cross-linked polymer is partially neutralized with a base and directed into a formation by a well. The esterified cross-linked inhibitor releases the inhibitor through hydrolysis of an ester which release is dictated by the extent of cross-linking, steric hindrance and temperature. The cross-linked inhibitor is said to be viscous but non-gelled.

SPE 64988 (prepared for the 2001 SPE International Symposium on Oilfield chemistry held in Houston, Texas, 13-16 February 2001) describes stable size-controlled microgels formed by crosslinking polymers under shear flow. It is said that these microgels are expected to control water mobility at long distances from wells to improve sweep efficiency and reduce selectively permeability to water for water production control. However, there is no suggestion that size-controlled microgels of cross-linked scale inhibitors can be formed under shear flow.

It has now been found that size-controlled microparticles of cross-linked scale inhibitor having a mean particle diameter of less than 1 micron may be formed under conditions of high shear or by comminution of a dried macrogel comprising cross-linked scale inhibitor. It has also been found that such size-controlled particles may be injected into a formation through an injection well and may propagate through the formation to the near-well region of a production well where the scale inhibitor is released through hydrolysis of the ester cross-links thereby inhibiting deposition of scale in the formation and/or in production lines downhole and at the surface.

Thus, in a first embodiment of the present invention there is provided particles of an esterifiable scale inhibitor cross-linked with a polyol via ester cross-links wherein the mean diameter of the particles is less than 1 micron.

The scale inhibitor is either carboxylic acid-containing or organophosphorus-

containing. Carboxylic acid-containing scale inhibitors are polymers based wholly or in part on an alpha,beta-ethylenically unsaturated carboxylic acid. Thus, suitable carboxylic acid-containing scale inhibitors include all homopolymers or copolymers (composed of two or more co-monomers) containing as one of its components, an alpha,beta-ethylenically unsaturated carboxylic acid such as acrylic acid, methacrylic acid, maleic acid, maleic anhydride, itaconic acid, fumaric acid, mesoconic acid and citraconic acid, and monoesters of dicarboxylic acids with alkanols having 1-8 carbon atoms. When the scale inhibitor is a copolymer, the other component monomer can be an alpha,beta-ethylenically unsaturated monomer containing a non-polar group such as styrene or olefinic monomers; an alpha,beta-ethylenically unsaturated monomer containing a polar functional group such as vinylacetate, vinyl chloride, vinyl alcohol, acrylate ester, acrylamide or acrylamide derivatives; and an alpha,beta-ethylenically unsaturated monomer containing an ionic functional group comprising methacrylic acid, maleic acid, styrenesulfonic acid, 2-acrylamido-2-methylpropane-sulfonic acid, vinylsulfonic acid, and vinylphosphonic acid. Suitable carboxylic acid-containing scale inhibitors include phosphino-polyacrylic acid polymers sold as Belsperse 161TM or Belasol S-29TM. The molecular weight range of the scale inhibitors utilized in this invention is from about 200 to about 20,000, preferably about 800 to about 10,000, more preferably about 1,000 to about 5,000.

Suitable organophosphorus-containing inhibitors include organophosphates, organophosphonates and polyphosphonates. Preferred organophosphorus containing inhibitors include alkyl ethoxylated phosphates; ethylenediaminetetramethylene phosphonic acid; aminotrimethylene phosphonic acid; hexamethylenediaminetetramethylene phosphonic acid; diethylenetriaminepentamethylene phosphonic acid; hydroxyethylidene diphosphonic acid and polyvinylphosphonic acid. Preferred organophosphorus compounds are described in U.S. Pat. Nos. 3,336,221 and 3,467,192. These patents are incorporated by reference herein.

Where the scale inhibitor is a copolymer comprising units derived from an alpha,beta-ethylenically unsaturated carboxylic acid and/or an alpha,beta-ethylenically unsaturated phosphonic acid, the mole % of such units in the copolymer is preferably in the range 1 to 99 mole %, most preferably in the range 10 to 90%.

Suitable polyols include all compounds containing two or more hydroxyl groups. These include ethylene glycol, glycerol and their higher homologs; dihydroxy-terminated polyethylene oxides or polypropylene oxides; polyvinyl alcohols of varying degrees of hydrolysis and molecular weight; modified polyvinyl alcohols or co-
5 polymers of vinyl alcohol. The molecular weight range of the polyol is from about 62 to several millions; preferably in the range 500 to 130,000, more preferably in the range 5,000 to 50,000, most preferably in the range 10,000 to 20,000.

The scale inhibitor is cross-linked with the polyol via esterification of the carboxylic acid and/or phosphonic acid in the scale inhibitor with the hydroxyl groups
10 in the polyol by heating a concentrate of the reactants in water in the presence of a strong acid catalyst. Preferably, the strong acid catalyst is selected from the group consisting of hydrochloric acid, sulfuric acid and trifluoromethane-sulfonic acid.

Suitably, the concentrate may be generated by introducing an aqueous solution of the esterifiable scale inhibitor and an aqueous solution of the polyol into a reaction
15 vessel. The reaction vessel may contain an aqueous solution of the strong acid catalyst. Alternatively, at least one of the aqueous solutions introduced into the reaction vessel may contain the strong acid catalyst. Suitably, the aqueous solution of esterifiable scale inhibitor and aqueous solution of polyol are introduced into the reaction zone in a ratio of from 10:90 to 90:10 by volume, preferably 30:70 to 70:30 by volume, most
20 preferably 45:55 to 55:45 by volume, for example 50:50 by volume.

Suitably, the concentration of esterifiable scale inhibitor in the concentrate is in the range 10 to 75 % by weight, preferably, 20 to 60% by weight.

Suitably, the concentration of polyol in the concentrate is in the range 1 to 25% by weight, preferably, 2.5 to 15% by weight, more preferably 5 to 10% by weight.

25 Suitably, the concentrate is heated to a temperature of 50° to 150°C. Typically, the esterification reaction is continued for about 6 to 60 hours, preferably 12 to 48 hours, more preferably 12 to 24 hours.

Typically, the concentration of acid in the concentrate is at least 0.5 M, preferably at least 1 M, more preferably at least 2 M, for example, at least 2.25 M.

30 Preferably, when the desired degree of esterification has been achieved, the product is partially neutralized with base to quench the esterification reaction.

Suitably, the reactor vessel may be operated under conditions of high shear in

which case the product of the esterification reaction is a microgel of the esterifiable scale inhibitor cross-linked with the polyol via ester cross-links wherein the microgel particles have a mean particle diameter of less than 1 micron.

Thus, according to a second embodiment of the present invention there is a provided a process for preparing a microgel of an esterifiable scale inhibitor cross-linked with a polyol via ester cross-links comprising:
reacting in a reactor vessel an esterifiable scale inhibitor with a polyol in the presence of a strong acid catalyst under conditions of high shear thereby cross-linking said scale inhibitor and forming a microgel having a mean particle diameter of less than 1
microns.

The reactor vessel may comprise any device suitable for mixing the concentrate under high shear so as to obtain a homogenous and reproducible microgel. Suitably, the high shear mixing device may be an UltraturraxTM, SilversonTM or CouetteTM mixer. Suitably, the shear rate in the reactor vessel is at least 0.5 ms^{-1} , preferably, at least 1 ms^{-1} , more preferably, at least 5 ms^{-1} , for example, at least 10 ms^{-1} .

Suitably, the particles of the microgel have a mean diameter of less than $1 \mu\text{m}$, preferably 100-750 nm, more preferably 200-500 nm, most preferably 200-300nm.

Preferably, the particles are present in the microgel in an amount of from 20 to 40 weight percent.

Preferably, the esterification reaction takes place in the presence of a surfactant in order to assist in dispersing the particles of the microgel. Suitable surfactants include water-soluble surfactants such as sodium dioctylsulfosuccinate, sodium N-oleyl-N-methyltaurate, sodium olefin(C_{14} - C_{16}) sulfonate, sodium polyoxyethylene lauryl sulfate, ethylenediamine alkoxlate block copolymer, 2,4,7,9-tetramethyl-5-decyne-4,7-diol ethoxylate, octylphenoxypolyethoxy ethanol, polydimethylsiloxane methylethoxylate, polyethoxylated oleyl alcohol, polyethoxylated castor oil, polyoxyethylene sorbitan monolaurate, polyoxyethylene sorbitan monooleate, polyoxyethylene dodecyl ether, polyoxyethylene lauryl alcohol, poly(oxyethylene-co-oxypropylene) block copolymer, poly(oxyethylene-co-oxypropylene) block polymer, p-[sonomyphenoxypoly(glycidol)], and cetyl trimethyl ammonium bromide and oil-soluble surfactants such as sorbitan monostearate, sorbitan monooleate, and octylphenol ethoxylate. Preferably, the concentration of surfactant in the concentrate is 0.01% to 1%, most preferably 0.05 to

1% by weight.

Preferably, the particles of the microgel may be coated, for example, with a polymer which dissipates in water or oil above a threshold temperature, for example, above a temperature of 75°C, 100°C or 125°C. Suitably, prior to its dissipation, the coating of polymer reduces the rate of diffusion of water into the particle and also the rate of diffusion of an aqueous solution of the scale inhibitor out of the particle.

Suitably, the polymers used for coating the particles of the microgel may be water-soluble polymers or oil-soluble polymers. Preferred water-soluble polymers for coating the particles of the microgel include polyacrylic acids; polymaleic acids; polyacrylamide; polymethacrylate; polyvinylsulphonates; copolymers of monomers selected from the group consisting of acrylic acid, maleic acid, acrylamide, methacrylate, 2-acrylamido-2-methylpropane-sulfonic acid, and vinylsulphonate; lignosulphonates; hydroxy methyl cellulose; carboxy methyl cellulose; carboxy methyl ethyl cellulose; hydroxy methyl ethyl cellulose; hydroxyl propyl methyl cellulose; methyl hydroxy propyl cellulose; sodium alginates; polyvinyl pyrrolidone; polyvinyl pyrrolidone acrylic acid co-polymers; polyvinyl pyrrolidone carolactam co-polymers; polyvinyl alcohol; polyphosphates, polystyrene-maleinates, poloxamers and poloxamines. Suitably, the poloxamers are linear ABA block co-polymers having the general structure $(EO)_n-(PO)_m-(EO)_n$ where n and m are integers and EO and PO represents structural units derived from ethylene oxide and propylene oxide respectively. Suitably, the poloxamines are ABA block co-polymers having a branched structure with a central ethylene diamine bridge i.e. $[(EO)_n-(PO)_m]_2-N-CH_2-CH_2-N-[(EO)_n-(PO)_m]_2$ where n, m, EO and PO have the same meaning as for the poloxamers. Preferably, the water-soluble polymer has a molecular weight in the range 1,000-100,000, preferably 5,000 to 30,000, for example, 15,000 to 25,000. Preferred oil-soluble polymers for coating the particles of the microgel include polyethers, polyamine derivatives or carbon backbone polymers having pendant nitrogen and/or oxygen atoms as described in EP 0902859 which is herein incorporated by reference.

The polymer may be added to the concentrate in the reactor vessel during the later stages of the esterification reaction. However, it is preferred to quench the esterification reaction, for example, with a base, before adding the polymer to the concentrate. Without wishing to be bound by any theory, the polymer will precipitate

onto the gelled particles and will at least partially coat the particles. Suitably, at least 75%, preferably, at least 90%, more preferably, at least 95% of the surface of the particles is coated with the polymer. Preferably, the coating is continuous (100% surface coverage). Preferably, the coating has a thickness of less than 30 nm,
5 preferably, less than 20 nm.

Suitably, the microgel can be concentrated by evaporation of the water phase to form a concentrated microgel. Preferably, the microgel particles are present in the concentrated microgel in an amount of from 30 to 50 weight %.

The microgel can also be dried, for example, by freeze drying or spray drying, to
10 form a dispersible powder comprising microparticles of the esterifiable scale inhibitor crosslinked with the polyol. Preferably, the microgel is dried by spraying the microgel onto a spinning heated disc. Without wishing to be bound by any theory, it is believed that, at least in the case of uncoated particles, the resulting dried particles may no longer be gelled i.e. any water incorporated into the particles may be removed during the
15 drying step thereby generating substantially anhydrous particles. In the absence of a coating, such substantially anhydrous particles will swell when redispersed in water. However, it is envisaged that such substantially anhydrous uncoated particles may be provided with an oil-soluble polymeric coating by adsorption of the oil soluble polymer, from solution in an organic solvent, onto the surface of the substantially anhydrous
20 particles. Suitable oil-soluble polymers for coating the substantially anhydrous particles include those described above. It is also envisaged that the uncoated particles may be coated with a water-soluble polymer by absorption of the water-soluble polymer from an aqueous solution thereof to form coated gelled particles. Suitable water-soluble polymers include those described above.

25 It is also envisaged that the esterification reaction may take place in a conventional stirred vessel operated under low shear conditions so as to form a macrogel of the esterifiable scale inhibitor cross-linked with a polyol. The resulting macrogel is then dried and the resulting solid is subsequently comminuted to give particles of cross-linked scale inhibitor having a mean particle diameter of less than 1
30 microns.

Thus, according to a third embodiment of the present invention, there is provided a process for preparing particles of an esterifiable scale inhibitor cross-linked

with a polyol via ester cross-links comprising the steps of:

- a) reacting an esterifiable scale inhibitor with a polyol in the presence of a strong acid catalyst in a reactor vessel under low shear conditions thereby forming a macrogel of the esterifiable scale inhibitor cross-linked with the polyol;
- 5 b) drying the macrogel to form a solid; and
- c) comminuting the solid to give particles of esterifiable scale inhibitor cross-linked with polyol having a mean particle diameter of less than 1 microns.

Suitably, in this embodiment of the present invention, the concentrate is stirred using, for example, a mechanical stirrer such as a paddle, an ultrasonic stirrer or by
10 bubbling an inert gas through the oil.

By macrogel is meant that the gel either does not comprise individual gelled particles or any individual gelled particles have a mean particle diameter which is substantially higher than 1 microns, for example, a mean particle diameter of above 100 microns.

15 By low shear conditions is meant the shear rate in the reactor vessel is less than 0.25 ms^{-1} , preferably, less than 0.1 ms^{-1} , more preferably less than 0.005 ms^{-1} , for example, less than 0.001 ms^{-1} .

Suitably, the reaction product of step (a) is allowed to settle such that the product separates into an upper water phase and a lower gel phase. The upper water
20 phase is then removed from the lower gel phase, for example, by decantation.

Suitably, the gel phase may be dried using any suitable drying technique for example, in an oven or by freeze drying or by spray drying. Suitably, the resulting solid is substantially anhydrous by which is meant that the solid preferably contains less than 0.1 % by weight of water, more preferably less than 0.05 % by weight of water.

25 Suitably, the comminuted particles have a mean diameter of less than 1 microns. Preferably, the comminuted particles have particle diameters in the range 100-750 nm, more preferably 200-500 nm, most preferably 200-300 nm.

The solid formed in step (b) may be comminuted using any suitable technique to obtain particles of the required size. Thus, the solid may be comminuted by jet-milling
30 or ball-milling or may be comminuted in a pulveriser, for example, a Fritsch pulveriser. Other suitable comminution techniques are described in Section 8 Perry's Chemical Engineers Handbook, 4th Edition, 1963, which is herein incorporated by reference.

Preferably, the solid may be comminuted by wet-milling, for example, in the presence of water or an oil, for example, diesel oil or kerosene, so as to mitigate the risk of agglomeration of the comminuted particles. Where the solid is comminuted by dry-milling or by wet-milling in the presence of an oil, the resulting particles are

5 substantially anhydrous. Where the solid is comminuted by wet-milling in the presence of water, the comminuted particles will swell in the water to form gelled particles.

Preferably, the solid is wet-milled in the presence of a surfactant so as to further mitigate the risk of agglomeration of the comminuted particles. Examples of suitable surfactants include those described above. The solid may also be comminuted in the

10 presence of a polymer which coats the exposed surfaces of the comminuted particles.

Without wishing to be bound by any theory, the polymeric coating reduces the rate at which water diffuses into and a solution of the scale inhibitor in water diffuses out of the comminuted particles. Preferably, the polymer has surface active properties and therefore also acts to mitigate the risk of agglomeration of the comminuted particles.

15 Suitable coating polymers include those described above.

In yet a further embodiment of the present invention there is provided a suspension comprising particles of an esterifiable scale inhibitor cross-linked with a polyol via ester cross-links dispersed in a liquid medium wherein the mean diameter of the particles is less than 1 micron.

20 The suspension may comprise particles prepared as described above.

The liquid medium may be an oil, an organic solvent or water, preferably water. Where the liquid medium is an oil, the oil may be kerosene, diesel, biodiesel, base oil or crude oil. Where the liquid medium is an organic solvent, it is preferred that the organic medium is a water dispersible solvent, for example, a mutual solvent such as methyl
25 butyl ether (MBE), ethylene glycol monobutyl ether (EGMBE), butyl glycol ether (BGE) or a biodegradable ester solvent such as Arrivasol TM. Where the liquid medium is water, the water may be fresh water, river water, aquifer water or sea water.

Suitably, the particles are dispersed in the liquid medium in an amount of from 20 to 50, preferably 30 to 50% by weight.

30 In yet a further embodiment of the process of the present invention there is provided a method of inhibiting scale formation in a subterranean formation comprising:

(a) injecting a suspension comprising particles of a scale inhibitor suspended in an aqueous medium into a formation through an injection well wherein the particles have a mean diameter of less than 1 micron;

5 (b) allowing the suspension to percolate through the subterranean formation towards a production well; and

(c) controllably releasing the scale inhibitor from the particles in the near well bore region of the production well.

10 By "near well bore region of the production well" is meant a radial distance of less than 100 feet, preferably less than 50 feet, more preferably, less than 30 feet from the well bore of the production well.

Preferably, the particles comprise an esterifiable scale inhibitor crosslinked with a polyol through ester cross-links with the scale inhibitor being controllably released in the near well bore region of the production well through hydrolysis of the ester cross-links

15 Suitably, the particles may be gelled particles which may be coated or uncoated (as described above) or coated anhydrous particles (as described above).

The rate of ester hydrolysis will be dependent upon both the temperature and the pH which the particles encounter in the formation. Typically, the suspension is injected down the injection well at a temperature of less than 10°C, for example 3 to 5°C.

20 Typically, the temperature of the subterranean formation in the near well bore region of the producing well is in the range 75-150°C. The temperature of the injected suspension will therefore increase as it percolates through the formation. The increase in temperature of the injected suspension with increasing radial distance from the injection well can be accurately determined (as would be well known to the man skilled in the art). The pH within the formation can also be readily determined. The molecular weights of the esterifiable scale inhibitor and/or of the polyol and the extent of crosslinking of the scale inhibitor can be controlled (for example, by controlling the concentration of the acid catalyst or the duration of the esterification reaction) so that the particles release substantially all of the scale inhibitor (through hydrolysis of the ester linkages) in the near well bore region of the production well. Suitably, the particles start to release the scale inhibitor through hydrolysis of the ester cross-links at a temperature of 50 to 150°C. Where necessary, the particles may be coated with a

coating which dissipates above a threshold temperature. Typically, the threshold temperature is less than the temperature of the near well bore region of the production well and is substantially above the temperature of the injected suspension. Suitably, the threshold temperature is at least 2.5°C below, preferably at least 5°C below, more preferably at least 10°C below the temperature of the near well bore region of the production well. Suitably, the particles may be coated with a coating comprising an oil or water dispersible polymer as described above.

Suitably, the suspension comprises particles of esterifiable scale inhibitor cross-linked with a polyol suspended in injection water (e.g. river water, aquifer water or seawater). The particles readily enter the porous formation and will travel through the formation together with the injection water.

Suitably, the suspension propagates through the formation at a rate of 15 to 100 feet per day. Typically, the temperature of the injected suspension increases at a rate of 1 to 10 °C per 100 feet in the radial direction from the injection well towards the production well. Suitably, the injection well is 0.25 to 1 mile from the production well.

Suitably, the particles start to release the scale inhibitor through hydrolysis of the ester cross-links at a temperature of 50 to 75°C.

Typically, a dispersible powder comprising cross-linked scale inhibitor particles having a mean particle diameter of less than 1 microns or a suspension comprising such particles suspended in a liquid medium is dosed into the injection water.

The dispersible powder or suspension may be continuously dosed into the injection water in which case the amount of cross-linked scale inhibitor particles in the injection water is selected so that substantially all of the scale inhibitor is released in the near well bore region to give an effective concentration of scale inhibitor. The amount of cross-linked scale inhibitor in the injection water is preferably in an amount in the range 0.1 to 2 weight percent, preferably 0.2 to 1 weight percent.

The dispersible powder or suspension may be intermittently dosed into the injection water in which case the dosage may be higher, preferably, 1 to 5 weight percent, more preferably 2 to 5 weight percent. Here the scale inhibitor is released from the particles in the near well bore region and at least in part adsorbs onto the surfaces of the porous rock formation. During intervals when the dispersible powder or suspension is not being dosed into the injection water, the scale inhibitor leaches from the surfaces

of the rock thereby maintaining an effective concentration of scale inhibitor for scale control. The amount of scale inhibitor released into the production water is preferably in the range 1 to 200 ppm.

It is also envisaged that a suspension comprising particles of esterifiable scale inhibitor cross-linked with a polyol via ester cross-links dispersed in a liquid medium (either an aqueous or organic liquid medium) and having a mean particle size of less than 1 micron, may be injected into a formation under pressure via a production well. The production well is then preferably shut-in for 2-50 hours, for example, 5-15 hours during which time the suspension percolates into the formation and the particles are believed to become trapped in the formation matrix. The scale inhibitor is released from the particles through hydrolysis of the ester cross-links under the conditions encountered in the near well bore region of the production well. After shut-in, the production well is returned on-stream. The produced fluids may be analyzed, for example, at the surface to monitor the concentration of scale inhibitor therein. Where the formation is oil-bearing, the shut-in process involving the introduction of the suspension may be optionally preceded by a pre-flush of the oil-bearing rock formation using an oil such as diesel, biodiesel, kerosene, base oil or crude oil. Introduction of the suspension may be followed by a subsequent separate step of over-flushing the production well with an oil. The oil used for the over-flush may be diesel, biodiesel, kerosene, base oil or oil produced by the well being treated. The amount of oil used for over-flushing the production well is suitably such that it reaches and flushes a target zone which is up to about 20 feet in a radial direction from the well bore. Suitably, the amount of oil used for the over-flush is in the range from 30 to 4000 bbls. Where the oil used for the over-flush is crude oil produced by the well being treated, the over-flush may be carried out in an inverse way e.g. as a back-sweep i.e. by making the crude oil as it emerges to the surface from the production well perform the function of the over-flush oil. After this period the crude oil production can be re-started.

The invention will now be illustrated by means of the following examples.

Example 1

Seawater (50g) and polyacrylic acid having a molecular weight of about 2,100 (30g) were introduced into a bottle and the resulting mixture was stirred using a magnetic stirrer until the polyacrylic acid was dissolved in the seawater. Polyvinyl

alcohol having a molecular weight of about 16,000 (2.5g; 98-98.8% hydrolysed) was ground into a fine powder and was then slowly added to the mixture in the bottle with rapid stirring. Stirring was continued until the polyvinylalcohol had dissolved.

5 The resulting concentrate was then heated to a temperature of between 85-90°C with rapid stirring using a magnetic follower. The concentrate was then rapidly stirred at this temperature for 4 hours. Fuming hydrochloric acid was then added (15-15.5g; 12.1 M) to the concentrate at a temperature of 85°C to initiate the esterification reaction. A free flowing fluffy white gel was formed. The gel was left to stir for 24 hours during which time the viscosity of the gel appeared to increase. The pH of the gel at the end of 10 the reaction was approximately 3. When cooled to room temperature the gel ceased 'flowing' and became notably more viscous.

Examples 2-4

Example 1 was repeated using 20g (Example 2), 35g (Example 3) and 40g (Example 4) of polyacrylic acid. In each case, sufficient fuming hydrochloric acid was 15 added to adjust the pH of the concentrate to approximately 3 at which point the concentrate turned cloudy. Between 18g-19g of fuming hydrochloric acid was added to the concentrate containing 20g of polyacrylic acid, between 19g-20g of fuming hydrochloric acid was added to the concentrate containing 35g of polyacrylic acid, and between 24g-25g of fuming hydrochloric acid was added to the concentrate containing 20 40g of polyacrylic acid.

With 20g of polyacrylic acid (Example 2), only a small amount of gel was formed. Using 30g of polyacrylic acid (Example 1) produced a very light gel in terms of both colour and density, whereas using higher concentrations such as 35g and 40g (Examples 3 and 4 respectively) produced a significantly greater volume of gel that was 25 darker in colour and higher in density than obtained with 20g of polyacrylic acid, which settled rapidly out of solution. For all polyacrylic acid concentrations, the supernatant liquid above the gel was observed to be cloudy. The cloudiness of the supernatant liquid was attributed to unreacted polyacrylic acid and polyvinyl alcohol.

For each Example, the supernatant liquid was separated from the macroscopic 30 gel by decantation. The wet solid was weighed and the dried in an extracted oven until the weight of the solid was constant. The solids were then reduced to powders using a variety of comminution methods: grinding in a mortar and pestle; pulverizing in a

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"Fritsch Pulverisette Type 14.702" pulveriser fitted with sieve ring sizes of 1.00mm and 0.2mm for between 20 minutes and 1 hour; and dry milling in a Retsch PM400 ball mill operated at 400 rpm for between 20 minutes and 1 hour. Following size reduction, the particles were then suspended in distilled water containing 0.02 g per ml of Tween 80
5 and then diluted into a larger volume of distilled water for particle sizing. The particle size of the suspension obtained in Example 4 was determined using a MicroTrac SRA 9200 laser particle sizer. The size distribution (volume weighted diameter) obtained was as follows:

D10 (μm) = 3.90

10 D50 (μm) = 19.60

D90 (μm) = 78.40

Examination of this suspension under a light microscope showed that the majority of the particles had diameters in the range of 3 to 6 μm .

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